BIOLEACHING OF MOLYBDENUM FROM A COAL LIQUEFACTION CATALYST RESIDUE

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ABSTRACT

Molybdenum disulfide, MoS_2, is used as a catalyst in coal-oil coprocessing. For most processes using molybdenum catalysts to be economical, the molybdenum must be recovered and recycled. Chemical recovery schemes have been devised, but typically recover only a fraction of the molybdenum. There are reports in the literature that bacteria can oxidatively solubilize MoS_2 (molybdenite) ore. This paper reports the initial results of experiments where Thiobacillus ferrooxidans are shown to microbially solubilize MoS_2 present in coal liquefaction catalyst residues. Small-scale shake-flask experiments show that after leaching of the catalyst residue by T. ferrooxidans at pH ~2 for 6-7 weeks, as much as 66-71% of the Mo can be solubilized. Analyses of the microbially-leached products and mass-balance calculations can account for 78-103% of the Mo initially present in the coal liquefaction residue.

INTRODUCTION

Molybdenum disulfide is used as a catalyst in coal-oil coprocessing. It is effective at concentrations as low as 200 ppm Mo by weight, based on coal (ref. 1). Molybdenum is added to the coal in the form of aqueous solutions of ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}$, or ammonium tetrathiomolybdate $(NH_4)_2MoS_4$. The MoS_2 catalyst is then formed in situ at coal liquefaction conditions at about 350°C, in the presence of hydrogen.

Even though MoS_2 is used at low concentrations, it is necessary to recover the molybdenum so that it can be recycled. A chemical recovery scheme has been developed (ref. 2). The coal liquefaction residue is first roasted (calcined). Under these conditions, the mineral matter in the residue and the molybdenum from the MoS_2 form compounds that are only partially soluble in the aqueous NH_3 used to leach the roasted material. This results in only a partial recovery of the molybdenum from the MoS_2 present in the coal-oil coprocessing liquefaction residue.

There are reports in the literature (refs. 3-7) that bacteria can oxidatively solubilize MoS_2 (molybdenite) ore. This paper reports on the use of Thiobacillus ferrooxidans to aerobically solubilize MoS_2 present in a coal liquefaction (coprocessing) catalyst residue to facilitate recovery of the molybdenum.

EXPERIMENTAL

Catalyst Residue: Two gallons of liquids produced from reaction of Illinois No. 6 hvB bituminous coal and Maya atmospheric tower bottoms under coprocessing conditions (ref. 1) were processed as shown in Figure 1. Approximately 100 grams of catalyst residue that contained MoS_2, obtained as the tetrahydrofuran-insolubles, were dried in a vacuum oven at 100°C for 4 hours and then ground to pass a 60-mesh screen. Analysis of the catalyst residue (done by Huffman Laboratories, Inc., Golden, Colorado) is given in Table 1.

Source of Microbes: Several strains of *Thiobacillus ferrooxidans* were obtained from the Center for Bioprocessing Technology of the Idaho National Engineering Laboratory (INEL). The original source of two of the strains (23270 and 13598P) was the American Type Culture Collection. Two other strains, A6 and PH, were obtained from Doris Thompson at INEL. The Bureau of Mines, Bruceton Research Center, provided a sample of acid mine drainage muck, which was designated as culture BOM and assumed to contain, inter alia, *T. ferrooxidans*.

In general, the several strains of *T. ferrooxidans* were maintained on 9K or INEL medium (see below). After the preliminary bioleaching experiments with catalyst residue were completed, inocula were taken from these finished experiments to start new bioleaching experiments. Thus, in some cases, the bacteria now being used have been exposed to catalyst residue and/or molybdate leachate solutions for as long as 6 months.

Preparation of Media: *T. ferrooxidans* grow optimally at pH 2.0-2.5. After some preliminary experiments, it was decided to use the 9K medium as described by Silverman and Lundgren (ref. 8). However, due to large amounts of ferric iron precipitates on the glassware with the use of 9K, most additional work was done with the INEL medium. The recipe (shown below) was obtained through Idaho National Engineering Laboratories, via Dr. Paul Wichlacz (ref. 9).

Recipe for INEL Salts

To 1 liter of distilled water adjusted to pH 2.0 with H_2SO_4, add:

$(NH_4)_2SO_4$	0.15 g
KCl	0.15 g
K_2HPO_4	0.15 g
$MgSO_4 \cdot 7H_2O$	3.36 g
$CaCl_2 \cdot 2H_2O$	1.28 g
$Al_2(SO_4)_3 \cdot 18H_2O$	2.25 g
$MnSO_4 \cdot H_2O$	0.12 g

200 mL of the solution is removed. Autoclave the remaining 800 mL portion in ten flasks (250 mL size) with 80 mL in each. Add 7.46 g of $FeSO_4 \cdot 7H_2O$ to the 200 mL portion while stirring. Filter sterilize the iron solution and add 20 mL aliquots to each 80 mL of sterile salts when cool.

Bioleaching experiments: The bioleaching experiments were carried out in 250 mL Erlenmeyer flasks on a shaker (125 rpm) in an incubator maintained at 29°C. Catalyst residue (0.5g) was added to 100 mL of medium (pH = 2). This mixture was then inoculated with 1 mL of the bacterial culture. After bacterial growth and leaching for 6-7 weeks, the microbially-treated sample was filtered and worked up as shown in Figure 2. The filtrates were analyzed for Mo by atomic absorption spectral analysis. The initial and final solid residues were analyzed for molybdenum as follows. First, the sample was ashed in a muffle furnace at 750°C. The ash was fluxed in lithium tetraborate and then dissolved in HCl. The HCl solution was analyzed by AA according to ASTM D3682-87.

RESULTS AND DISCUSSION

Results from small-scale shake-flask experiments are shown in Table 2. The dates that the experiments were run are given in parentheses above the column headings. In these shake-flask experiments, which demonstrate the feasibility of bioleaching MoS_2, as much as 71% of the Mo initially present in the catalyst residue was solubilized. Results of the control experiments given in Table 2 show that the amounts of Mo solubilized in the controls are low compared to amounts of Mo solubilized in the microbial leaching experiments. In order to estimate the overall precision in these experiments, values calculated for the mass balance for molybdenum are also shown in the sixth row of the table. For the experiments described in Table 2, the amount of Mo found by analysis of solutions B and D and of residue E (see Figure 2) could account for 78 to 103% of the molybdenum present in the original catalyst residue A.

These initial experiments, which show that some strains of Thiobacillus ferrooxidans can solubilize MoS_2 when it is present in a residue from coal-oil coprocessing, also show that the other materials present in the residue do not stop the bioleaching of the molybdenum. It is interesting to note that molybdate concentrations in solution at the end of the experiments were as high as 51 ppm. Reports in the literature (refs. 4-7, 10-12) suggest that a concentration as low as 10 ppm molybdate is toxic to T. ferrooxidans. However, inocula taken from these high concentration molybdate flasks, and used in subsequent experiments, proved viable and capable of additional bioleaching. This would suggest that we have developed a strain of T. ferrooxidans that has adapted to high molybdate concentrations. But also, it is possible that the condition designated as "toxic" to the bacteria might be better described as "inhibitory."

Both media used (9K and INEL) contain ferrous iron, as does the liquefaction catalyst residue. After bio-oxidation, this results in relatively high concentrations of ferric iron in the leachate solutions. We hypothesize that the iron(III) species present in solution form insoluble iron(III)molybdate compounds, as depicted in Figure 2. After the microbially-leached solutions are filtered, the iron(III) molybdate present (mixed with the unreacted catalyst residue in mixtures) was dissolved in 3N HCl. After filtration, this HCl solution (acid extract D) contains most of the molybdate that was formed during the bioleaching. In the best result, solutions B and D together contain 71% of the Mo solubilized from the MoS_2 initially present in the catalyst residue.

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DISCLAIMER

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TABLE 1. Analysis of the THF-Insoluble MoS_2/Co-Processing Residue

Element	Percent
Carbon	24.5
Hydrogen	1.95
Oxygen (Direct)	7.2
Nitrogen	0.72
Sulfur	7.4
Iron	9.9
Molybdenum	2.80

TABLE 2. Results of Shake-Flask Bioleaching Experiments Using 0.5 Gram MoS_2 Catalyst Residue

	9K Experiments (7/26 - 9/8)				INEL Experiments (8/17 - 10/4)						Bioleaching Group #5	
Inoculum Medium	23270 + 9K	13598P + 9K	UNINOC 9K	23270 + Salts (9K)	13598P + INEL	23270 + INEL	PH + INEL	A6 + 9K	BOM + 9K	UNINOC + INEL	13598P + INEL	23270 + INEL
Mo Conc., Filtrate B (ppm)	40	43	0.3	47	51	39	0.5	0.1	33	2.3	34	31
Mo in Filtrate B (mg)	2.71	3.00	0.02	1.89	4.32	3.45	0.04	.01	2.28	0.15	2.46	2.25
Mo in Acid-Extract D (mg)	3.36	4.13	1.13	3.26	5.64	5.82	1.44	1.38	3.36	1.26	6.15	6.11
Mo in Acid-Extract Residue E (%)	1.65	1.70	3.16	2.19	1.40	1.22	2.80	2.65	2.25	3.06	1.20	1.31
Mo in Acid-Extract Residue E (mg)	5.91	5.98	11.22	6.24	4.58	3.84	9.38	8.93	7.43	9.85	3.92	4.20
Mo Recovery (%)	85	94	88	81	103	94	78	74	93	80	90	90
Mo Solubilized (%)	43	51	8	37	71	66	11	10	40	10	62	60

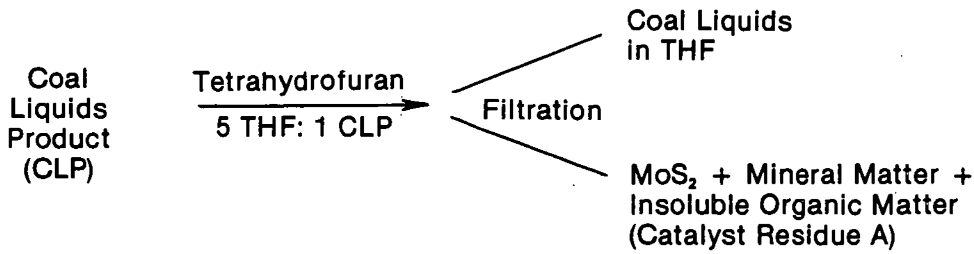

FIGURE 1. SEPARATION OF MoS_2 CATALYST RESIDUE FROM COAL-OIL CO-PROCESSING LIQUIDS.

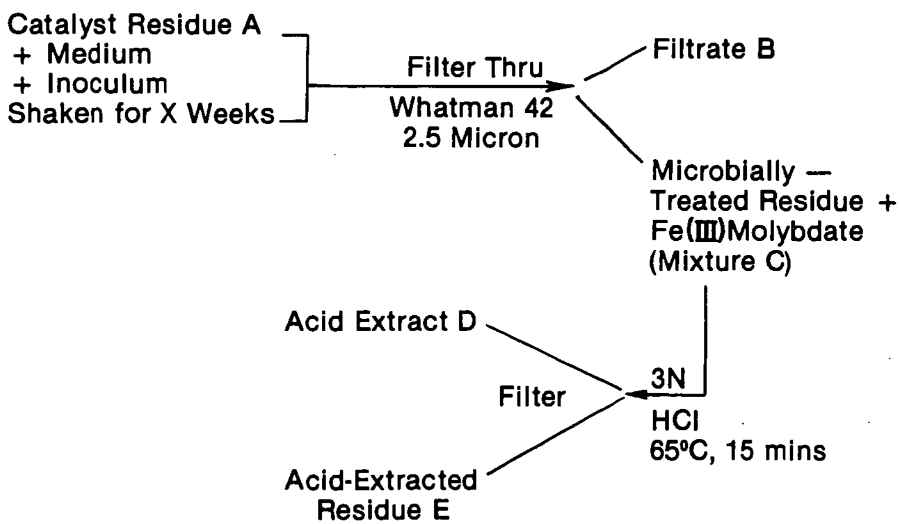

FIGURE 2. SHAKE-FLASK BIOLEACHING OF MoS_2 CATALYST RESIDUE: MASS BALANCE EXPERIMENTS.